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APPLICATION OF ZIRCONIUM NANOPOWDER IN HYDROGEN ENERGY

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Abstract: The general results of researches of interaction of zirconium nanopowders with water are presented. It is proved that in the conditions of rather low temperatures, nanopowder of zirconium interacts with water, emitting gaseous hydrogen. Process of interaction is followed by chemical effects, fall of water temperature. Advantages and disadvantages of use of zirconium nanopowder for hydrogen production in the industry are found out.

Keywords: nanozirconium, hydrogen energy, radiolysis, thermolysis

1. Introduction

The main problem of the present – finding of new power sources which shortly would replace oil, gas and coal which reserves, according to experts, were exhausted in the next years. In recent years nuclear power intensively develops. Intensive growth of nuclear power creates a problem of burial of radioactive waste. One of the main projects of waste disposal is their clarification from Earth and sending by means of spacecrafts towards the Sun as accumulation of waste on Earth leads to growth of incidence of the population. Now, such project demands an investment of large sums. According to forecasts of experts, the conceived project will be carried out through 100÷200 years. Perhaps, powerful sources of electric energy will be created.

Problems of hydrogen power

The most studied direction among technologies of receiving and transportation of energy - is the hydrogen power (HP) and hydrogen which is characterized by the following features [1-10]:
- in the nature an amount of hydrogen is much, mostly in water;
- H_2 is the easiest element therefore has high power consumption counting on unit of mass – 121 MJ/kg;
- a product of oxidation (combustion) of H_2 is H_2O – ecologically the safest and clean product;

The interesting idea is receiving of H_2 in a solid form under strong pressure when cooling. We plan to receive firm H_2 by cooling of gaseous H_2 which density reaches to 2000kg/m^3, and stability – to 2000^{0}C. Unfortunately, experimental works weren't crowned with success so far. Receiving of firm H_2 will give the chance to solve many problems of hydrogen energetic, rocket production and organic synthesis. Among the known gases, hydrogen has the highest viscosity and high heat conductivity. At the room temperature and atmospheric pressure, heat conductivity of hydrogen – 0.182 W / (m • K) that is 1.24 times higher than heat conductivity of helium, 5.9 times higher than methane, 10.7 times higher than argon, 7.2 times higher than nitrogen and oxygen. The coefficient of dynamic viscosity of gaseous hydrogen makes $8.92 \cdot 10^{-6}$ Pa•s with that is 2.11 times lower, than at helium in the same conditions. By means of this circumstance, hydrogen is effectively applied to reduction of friction and cooling in moving parts of devices (in turbo generators of thermal and nuclear power). The low viscosity of hydrogen increases probability of leaks through consolidations that toughens requirements to quality of the hydrogen gas equipment.

The existing ways of production of hydrogen are based on use as initial raw materials of water (electrolysis, photolysis and radiolysis), natural gas and coal (steam and steam-oxygen conversion), hydrogen sulfide (chemical and plasma chemical decomposition) and also many other substances [11,12].

The most perspective technology of receiving of hydrogen in the future – is electrolysis of water [12-13]. Important features of electrolysis of water – ecological purity, a possibility of creation of devices with a wide range of productivity, high purity of the produced hydrogen, existence of an environmentally friendly and valuable by-product (gaseous oxygen).

Hydrogen is one of the combustible gases with the increased potential of explosion. He has wide concentration limits of burning and a detonation, high speed of distribution of a flame (is 8 times higher, than at methane) and also low (is 14.5 times lower, than at methane) energy of ignition. The low density and high speed of diffusion of hydrogen promotes fast decrease in its concentration on the open area and in the ventilated rooms. Besides hydrogen has the high lower bound of a detonation (2.06 times higher, than at methane) that significantly reduces its potential of explosion in actual practice.

The concept to environmentally friendly hydrogen power includes:

- Production of hydrogen from water with use of nonrenewable sources of energy (hydrocarbons, atomic energy, thermonuclear energy);
- production of hydrogen with use of renewable sources of energy (the sun, wind, energy of sea inflows, biomass);
- reliable transportation and storage of hydrogen;
- wide use of hydrogen in the industry, on transport (unearthly, air, water and underwater), in life;
- ensuring reliability of materials and safety of hydrogen power systems [4,11-12].

Hydrogen is not a power source, but this means of transformation of other power sources to chemical energy in the form of the reserved pure hydrogen which can be used subsequently at his oxidation. Hydrogen needs to be made and transformed for obtaining final energy. Now in the world it is receives 96% of final energy from fossil fuel, mainly from oil, and carbon is still transferred to CO_2 so it doesn't solve a problem of emissions.

In the United States 90% of pure hydrogen turn out from natural gas, with the efficiency of use of 72%. It means that 28% of the energy which is contained in natural gas – methane, is lost, apart from energy which is spent for production and transportation of natural gas to the plant producing hydrogen. Only 4% of hydrogen receives from water by means of electrolysis. Cost of production of hydrogen from water (different types of electrolysis) is 3 - 6 times higher, than receiving of hydrogen from natural gas. This method is used only when it is necessary to receive especially pure hydrogen [10].

2. Methods of hydrogen production

Now receiving of hydrogen from natural organic fuels is widely studied. The main technologies are:

- steam conversion of methane;
- partial oxidation of methane;
- coal gasification;
- alternative methods of hydrogen production;
- receiving of hydrogen in solid-state electrochemical devices.

Receiving of hydrogen and operations on hydrogen power engineering belong to the priority directions of social and economic development. Judging by the modern rates and scales of development of hydrogen power engineering, the world civilization will pass to hydrogen economy in the nearest future. The main objective is creation of fuel elements and use of hydrogen for obtaining of electrical energy. The active search is carried for finding of new ways of the translation of power-intensive industries, including transport on the basis of use of the fuel elements (FE). A progress in the development of power stations is pinned on the hope for a solution of the problem of mankind support by renewable environmentally friendly energy resources and also a possibility of change and enhancement of system of power supply of different objects – from cell phones, computers, cars to houses, the large industrial enterprises and in general the cities on the basis of FE [10].

The fuel element is an electrochemical source of current in which direct transformation of energy of fuel into electric energy is carried out. It is very important that there is no transformation of chemical fuel into mechanical and thermal energy and also there is no transformation of heat at these devices. Therefore power efficiency is much higher, than at traditional power stations and can be up to 90% [13].

Chemical reactions take place in FE on special porous electrodes (the anode and the cathode) activated by palladium where the chemical energy reserved in hydrogen and oxygen will effectively be transformed to electric energy. Hydrogen is oxidized on the anode, and oxygen is restored on the cathode. There are various types of FE. They are usually classified by the used fuel, working pressure and by the nature of application. Hydrogen is considered the main source of fuel for FE though process of transformation of fuel allows extracting hydrogen from other his types also, including methanol, natural gas, oil, etc. Unlike the accumulator and batteries, FE isn't exhausted and doesn't demand a recharge; he works while fuel moves.

The main reactions in low-temperature fuel elements – are cathode restoration of oxygen and anode oxidation of hydrogen and plain alcohols. In polymeric FE he usually represents a proton exchange membrane where one side is covered by cathode, and another – by anode catalysts. For increase in a specific surface of the catalyst and decrease in a consumption of metal the high-disperse carrier (carbon nano-materials) is used and also special methods of receiving of metal nano-powders are developed.

Now zirconium and systems on its basis should be considered the most suitable catalyst for these reactions, especially in FE with solid polymeric electrolyte. The prevalence of zirconium in crust is twice higher, than platinum, palladium and gold. The cost of zirconium is most considerable among other metals. In this regard active researches on decrease in an expense of Zr are conducted. Thus, the fuel element consists of the ionic conductor (electrolyte) and two electrodes. In recent years the steady tendency of transition from classical fuel elements with liquid electrolyte completely to solid-state is observed. And still the hydrogen power already lives and prospers. It means technologies of conversion of hydrocarbons – first of all hydro cracking and also production of synthetic oil and motor fuels (GTL – gas – to – liquid, gasification of coals, etc.). Formation of synthesis – gas (mix of hydrogen and the carbon monoxide) from water and hydrocarbon fuel (HC) and the subsequent synthesis of other hydrocarbon is the cornerstone of the majority of the listed technologies:

$$HC_1 + H_2O \rightarrow H_2 + CO \rightarrow HC_2 + \dots$$

Process of transformation of natural gas into middle distillates – diesel fuel, kerosene, gasoline – is based on the Phisher — Tropsh (PT) technology developed in the 20th years of the last century. Only 5-6 years ago this technology was considered as very expensive and exotic, being of purely academic interest. Now it is one of the most perspective power technologies. Transformation came thanks to developments of new highly effective catalysts and improvement of PT technology at a receiving stage of an intermediate product – synthesis – gas from natural gas therefore the price of the final synthesized oil products became much lower (about 20 dollars for barrel) and approached cost value of natural oil [10].

It should be noted that there is a set of the interesting and perspective directions of development and use of technologies of hydrocarbons conversion with use of synthesis – gas. For example:

- conversion of coal in methane directly in layer;
- mini oil refineries with hydrocarbon conversion which can be put on bushes of nearby

wells for the purpose of transformation of methane, condensed gas, associated gas, condensate and oil:

a) to better synthetic oil or gas, on structure close to natural;
b) to the methanol developing at the same time the electric power, etc.

The main converter of hydrogen in energy are low – and high-temperature fuel elements. By the present moment the reached efficiency of industrial low-temperature hydrogen elements doesn't exceed 40-50% that in total with losses of energy on receiving of hydrogen doesn't allow to speak about a significant gain in efficiency of use of energy in comparison with the traditional internal combustion engine or the diesel.

Decrease in emissions of CO_2 as main objective of hydrogen power also not indisputably. It isn't finalized yet that the existing warming of climate is connected only with emission of greenhouse gases. Perhaps, the major role in this process is played by the average power of radiation of the Sun. Many calculations show in the present article that a full production cycle, including production of hydrogen, and not just his use, not only doesn't reduce total emission of CO_2 and others greenhouse gases, but considerably increases this emission in comparison even with traditional technologies [11].

In such areas of the equipment as aircraft, especially military, space, shipbuilding, some elements of hydrogen power have already found the place thanks to enormous short-term power giving in the required timepoints and to other their unique opportunities. Possibly, these technology solutions will be used further.

Interesting properties of nanozirconium

Metal Zr – one of active metals, is always covered with a thin continuous oxidic film which protects metal from interaction with oxygen, water vapors and diluted solutions [1,3]. When processing nanozirconium by alkalis and acids, an integrity of an oxidic film breaks and then Zr begins to interact with water actively. The equation of reaction of Zr with water, it is possible to present as follows:

$$Zr + 2H_2O = ZrO_2 + 2H_2 \quad (1)$$

It turns out that at interaction of one Zr atom with water two molecules of H_2 are formed, at interaction of 91 g of Zr with water – 44,8l (4 g) of H_2 and 123 g of ZrO_2 is formed. Rate of this reaction at the room temperature is not high because a dissolved oxygen presents at water always. Increase in temperature and also presence of small amounts of alkalis, salts and acids in water causes to increase of the rate of reaction.

Reaction of Zr with H_2O – is exothermic as during interaction warmth is distinguished. As show our calculations, at full interaction of 91 g of Zr (1 mol) with H_2O and formation of ZrO_2 and H_2 on reaction (1), 6530 kJ of warmth are allocated. Depending on a ratio of the masses of taken Zr and H_2O and also the reaction rate (rate of production of warmth) and heat removal speed in the environment, reactionary mix can have rather constant temperature and can gradually heat up that, in turn leads to increase of rate of reaction. The minimum mass of H_2O necessary for full expenditure of 91 g of Zr with formation of products is 123 g. The allocated amount of heat is enough for heating of products of reaction to $t=2300^0$ C. A small amount of water leads to sharp fall of temperature due to heating of this excess amount of water.

The fact of formation of the hollow spheres consisting of Zr oxides of various modifications is explained by the following signs. Thickness of an oxidic cover on a surface of nanoparticles of Zr – uneven and therefore interaction of Zr begins with H_2O in those places where this cover thinner. Particle movement on such site of a surface is complicated and minimum during interaction that is why the front of reaction develops unevenly and the particle "is more etched" from the specified site. As a result at expenditure of Zr a nanoparticle lefts only one cover - "shell".

It is established that products with such morphology turn out in rather soft conditions – at rather big surplus of H_2O and temperature of the reactionary mix which isn't exceeding 70^0C. Temperature increase at mix promotes to destruction of hollow structures and formation of products with cellular structure.

The formed splinters of an oxide-hydroxide cover have an appearance of shells. From the point of view of H_2 generation, the chemical and mechanical effect promotes sharp increase in rate of reaction. The rupture of an oxide-hydroxide cover leads to penetration of H_2O directly to the surface of metal. H_2 is formed on the metal-metal oxide (hydroxide) border and has high temperature – the self-heating temperature which is hundreds of degrees. At 400^0C H_2 effectively penetrates through a 10 cm thick plate of nickel.

Complex use of products of interaction of Zr nanopowders (NP) with H_2O, effective functioning of a power cycle, utilization of heat on the basis of Zr NP is a real technology of receiving of gaseous hydrogen. Application of Zr NP gives us indisputable advantages: need for storage and transportation of gaseous H2 disappears that raises explosion safety of hydrogen power (HP).

Now application of Zr NP in mobile small-size sources of hydrogen is relevant: for hybrid automobile engines, use in hard to reach areas (the massif, deserts, the tundra). Zr NP can be basis of HP for settlements on the Moon and H_2 source in fuel cells for the expeditions directed to Mars. Thus the problem of technical character – development of the mobile sources of H_2 combined with fuel cells which are necessary for development of electrical energy is on the agenda.

Therefore studying of properties of NP of zirconium under influence of γ – radiation is of practical and scientific interest [14-17].

The kinetics of accumulation of molecular hydrogen at a heterogeneous radiolysis of water in nano-Zr+H_2O_{liq} and nano-Zr+H_2O_{vap} systems is studied. Nano-Zr as constructional material, has radiation firmness and working capacity in nuclear reactors. The radiation and catalytic activity of nano-Zr is defined by two methods as it has been specified in an experimental part. In fig. 1 the kinetic curves of molecular hydrogen accumulation at a heterogeneous radiolysis of water are given in the presence of nano-Zr in two states. From initial linear parts of kinetic curves, values of accumulation rates and a radiation-chemical yield of hydrogen in the studied systems are defined [17].

On the kinetic curve shown in fig. 1 (a) it is possible to allocate two sites:

I – area which is characterized by rather high rate of accumulation of hydrogen on initial line sections;
II-rather slow stage of accumulation of molecular hydrogen.

On the kinetic curve shown in fig. 1(b) it is possible to consider growth of accumulation rate of molecular hydrogen. It once again demonstrates that in the process of water decomposition not only the energy carriers received on the basis of zonal transitions, but also δ-electrons with small energy and the emitted electrons participate. Therefore, finally a hydrogen yield in nano-Zr+ H_2O_{liq} is more, than in nano-Zr+H_2O_{vap}. From the table it is visible that at a heterogeneous radiolysis of water in a condition of a full covering of a layer of nano-zirconium (nano-Zr+H_2O_{liq}), the observed values of a radiation-chemical yield of hydrogen in ~5.4 times more than at a heterogeneous radiolysis of water in the adsorbed state on the surface of nano-zirconium. It demonstrates that in case of nano-zirconium in volume of water, there is an effective transfer of energy from a firm phase to molecules of water [17].

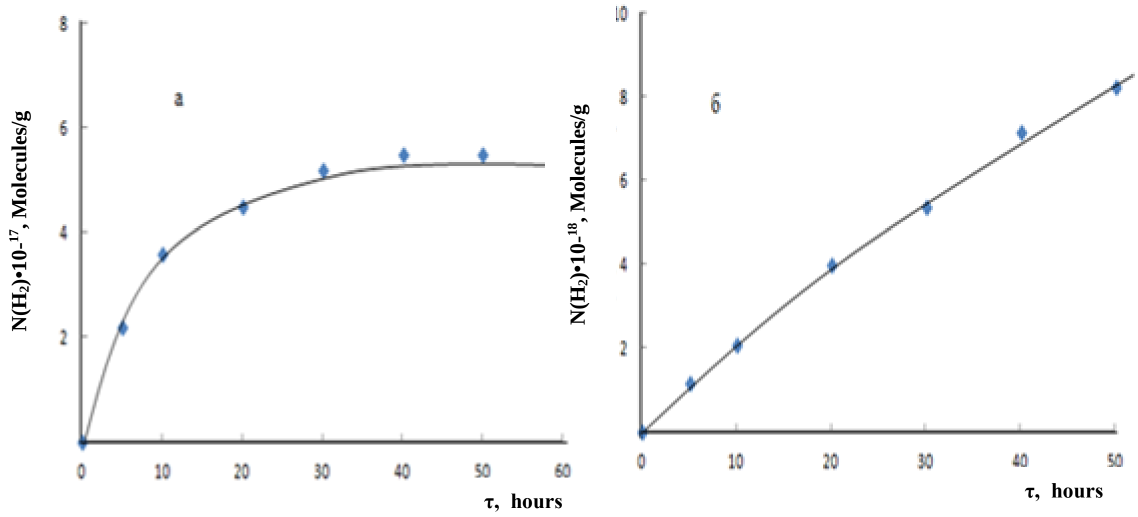

Fig.1. A kinetic curve of formation of molecular hydrogen at radiation and heterogeneous decomposition of water in nano Zr+ H_2O_{liq} (a), nano-Zr+H_2O_{vap} (b)systems at T=300K, D=0,15 Gy/s.

Table1: *Values of accumulation rates and radiation chemical yields of molecular hydrogen at a radiation and heterogeneous radiolysis of water in two states at T=300K*

№	Irradiated systems	$W(H_2)$, molecules· g^{-1} s^{-1}	$G(H_2)$, molecules/100eV
1.	$Zr+H_2O_{ads}$	$1{,}22\cdot10^{13}$	1,3
2.	$Zr+H_2O_{liq}$	$6{,}67\cdot10^{13}$	7,1

Existence on kinetic curves the second slow stage of a radiolysis demonstrates that there is diffusive complicated stage of a heterogeneous radiolysis of water in the presence of nano-zirconium at T=300K. Influences of temperature on rates of molecular hydrogen formation at a heterogeneous radiolysis of water are studied on the example of the nano-Zr+H_2O_s systems as temperature increase in nano-Zr+H_2O_{liq} system in the closed ampoules is experimentally impossible.

3. Conclusions

From the given results it is visible that nanostructure materials acquire an important role in nuclear power as constructional and functional materials practically at all stages of a nuclear fuel cycle. It is extremely important formation of ordered nanostructure of new phases with the period in several nanometers in irradiated nanostructure materials which promote maintaining properties of materials in case of high-dose radiation. The found phenomenon is the beginning of development of the new direction of radiation materials science – creation of the constructional materials "positively" reacting to a factor of irradiative effects.

Application of nanotechnologies and hydrogen power engineering in nuclear area, are connected to creation of nanostructure materials and coverings of constructional elements of the NPP and future TNR (thermal nuclear reactor) for the purpose of increase in hardness of corrosion and radiation resistance.

Other applications of nanotechnologies in power engineering: solar batteries, chemical transformers of energy, new sources of storage of energy, reactors on processing of hydrocarbon raw materials in hydrogen fuel, hydrogen stores (nanotubes) in hydrogen power engineering.

Transition to nanostructure materials will allow to create materials for nuclear power engineering with qualitatively new properties and to create the new directions of development of the energetic equipment. Therefore the relevant task is the accelerated development of operations in the field of nanotechnologies and nanomaterials.

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ПРИМЕНЕНИЕ НАНОПОРОШКА ЦИРКОНИЯ В ВОДОРОДНОЙ ЭНЕРГЕТИКЕ

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Резюме: Представлены общие результаты исследований взаимодействия нанопорошков циркония с водой. Доказано, что в условиях относительно невысоких температур, нанопорошок циркония взаимодействует с водой, выделяя газообразный водород. Процесс взаимодействия сопровождается химическими эффектами, понижением температуры воды. Выяснены преимущества и недостатки применения нанопорошка циркония для получения водорода в промышленности.

Ключевые слова: наноцирконий, радиолиз, водородная энергетика, термолиз

HİDROGEN İSTEHSALINDA SİRKONİUM NANOTOZUNUN TƏTBİQİ

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Xülasə: Sirkonium nanotozunun su ilə qarşılıqlı təsirinin ümumi nəticələrinə dair məlumatlar təqdim edilmişdir. Sübut edilmişdir ki, nisbətən aşağı temperaturda sirkonium nanotozunun su ilə qarşılıqlı təması zamanı hidrogen qazı azad olunur. Qarşılıqlı təsir prosesi kimyəvi çevrilmələr və suyun hərarətinin azalması ilə müşayiət olunur. Sənayedə sirkonium nanotozunun hidrogen istehsalı üçün istifadə edilməsinin üstünlükləri və çatışmamazlıqları aydınlaşdırılmışdır.

Açar sözlər: nanosirkonium, radioliz, hidrogen enerjisi, termoliz